Permeability Studies Applied to Grain Boundary Diffusion in Alumina Scales

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Alumina Scale Growth Mechanisms: Signposts along a 40 year journey

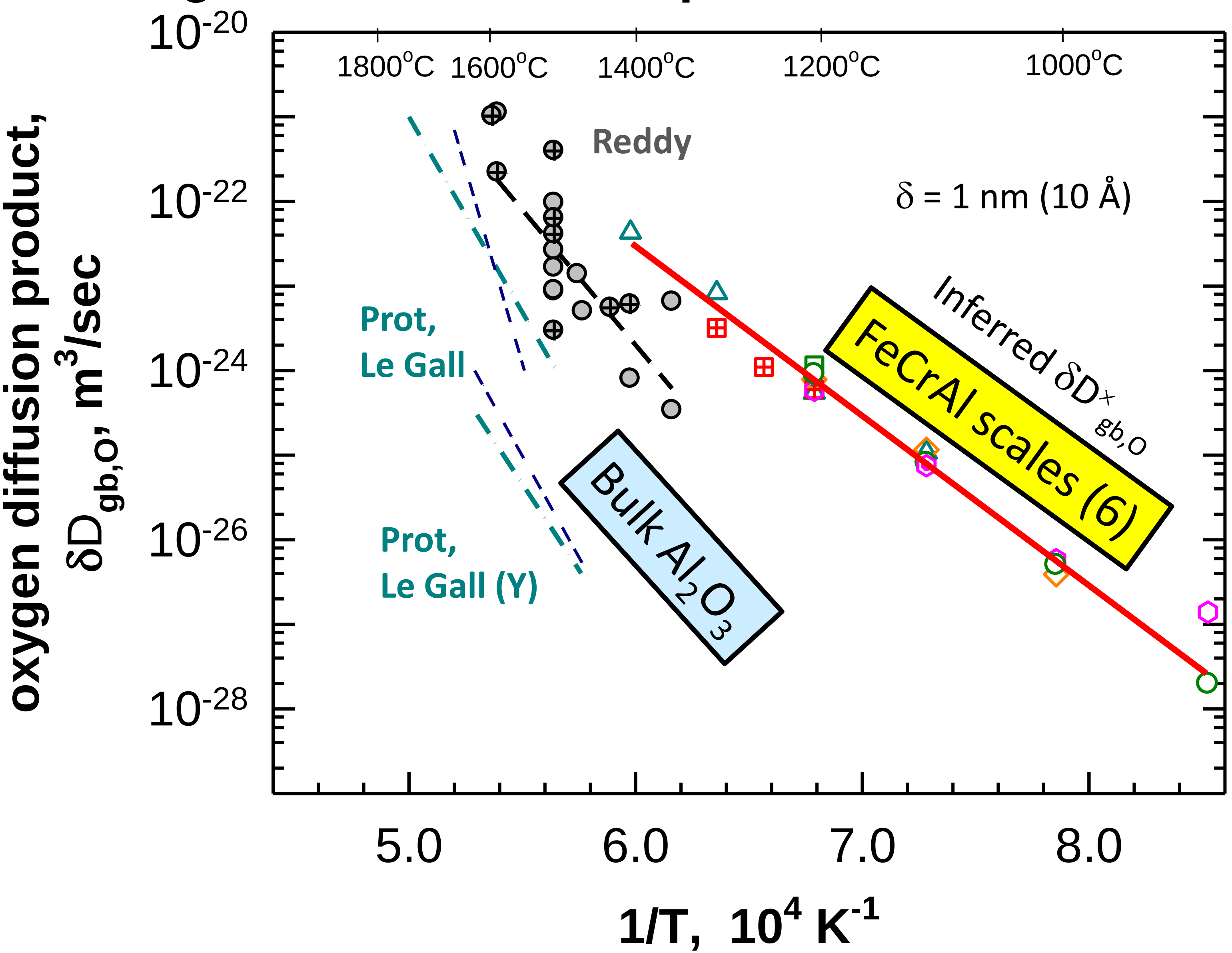
1. **Bulk** Al_2O_3 vs Al_2O_3 **scale** diffusivity
2. **Oxygen** inward vs **Aluminum** outward (n-type vs p-type)
3. Short circuit **grain boundary** diffusion (grain growth)
4. ‘cubic’ or **sub-parabolic** growth rates
5. **^{18}O tracer** (double oxidation) studies (NRA, SIMS profiles)
6. **Activation energies** (Arrhenius plots of log k_p vs 1/T)
7. Growth **stress**; creep relaxation
8. **Dopant** effects on defects, transport, and morphology
9. **pO_2** effects on σ_{el} , σ_I, $[V_o^{\circ\circ}]$, $[V_{Al}'''$], D_O, D_{Al}

Objectives

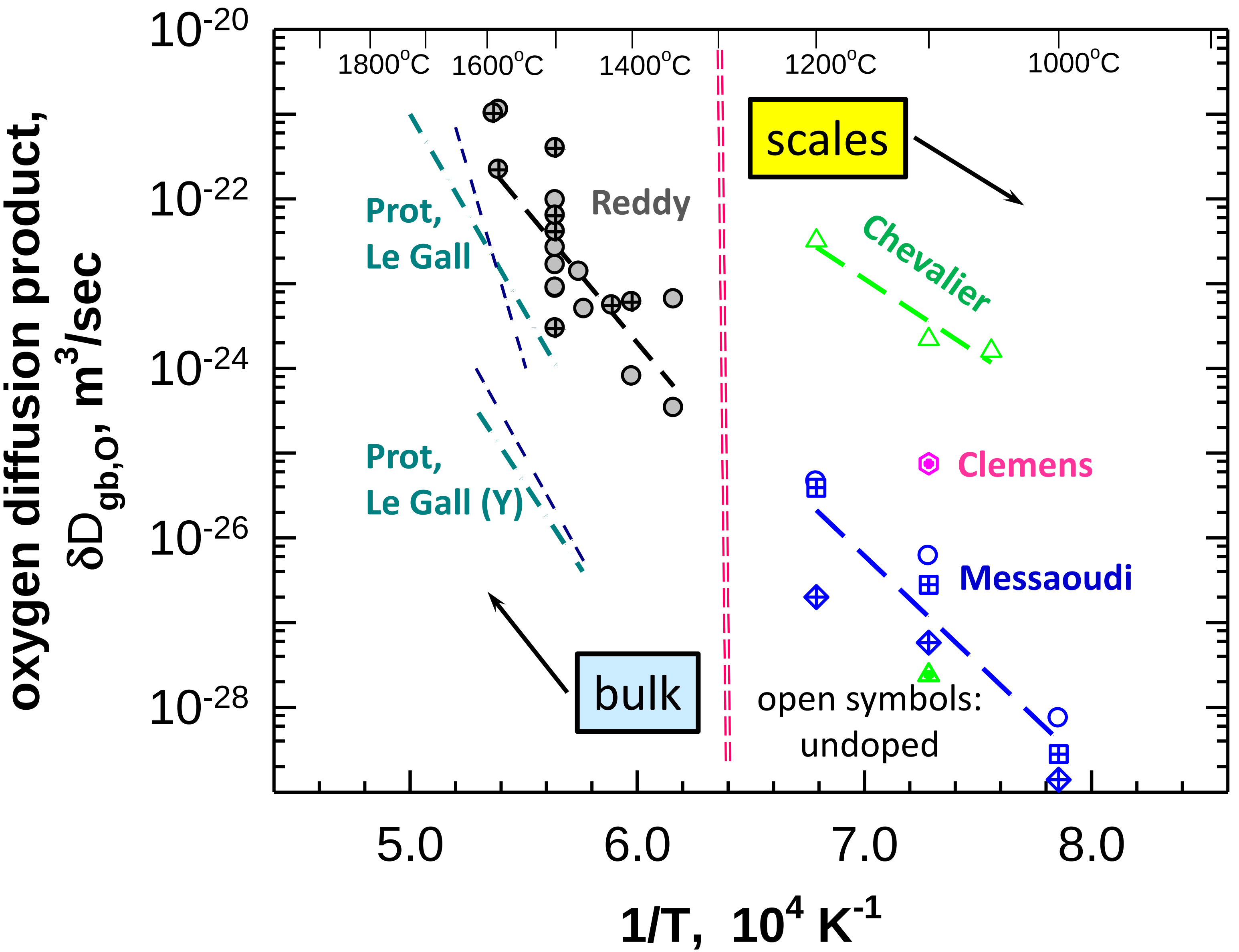
- Introduce permeability, $\delta D_{gb,O,Al}$ equations
- New Wagner solutions
- Compare $k_{p,i}$ (predicted, measured, literature)
- Compare $\delta D_{gb,O}$
  predicted: permeability vs oxidation
  measured: ^{18}O literature)
- Recap, new insights
- Epilogue: MDC150L Ni(Pt)Al coating

Alumina Grain Boundary Diffusivity Product

Wagner Oxidation Compared to Bulk ^{18}O Tracer



Alumina Grain Boundary Diffusivity Product
^{18}O Tracer: Bulk Compared to Oxidation



Wagner Model (from Kofstad)

$$k_{p,\text{instant}} = 2x\frac{dx}{dt} = \int_{P_{O_2},\text{interface}}^{P_{O_2},gas} \left(3/2D_{eff,Al} + D_{eff,O}\right) d\ln P_{O_2}$$

GOAL: $k_p \leftrightarrow D_{Al,\,O}(Al_2O_3)$

Grain Size Affects D_{eff}

$$D_{eff} = (1 - f)D_l + f(D_{gb})$$

$$D_{eff} \approx fD_{gb} = \frac{2\delta D_{gb}}{G_i}$$

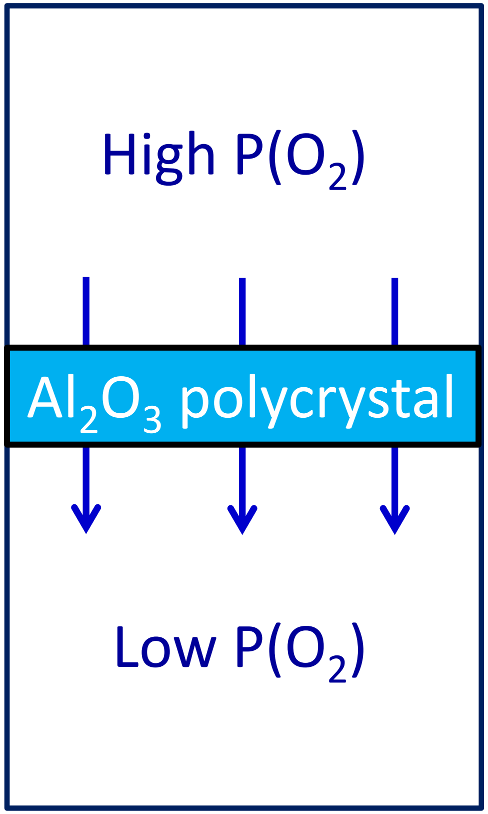
$$G_i\ (grain\ size) \propto T, t$$

Alumina Permeability Studies:

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839

1-10^5 Pa
(Ar-O_2)

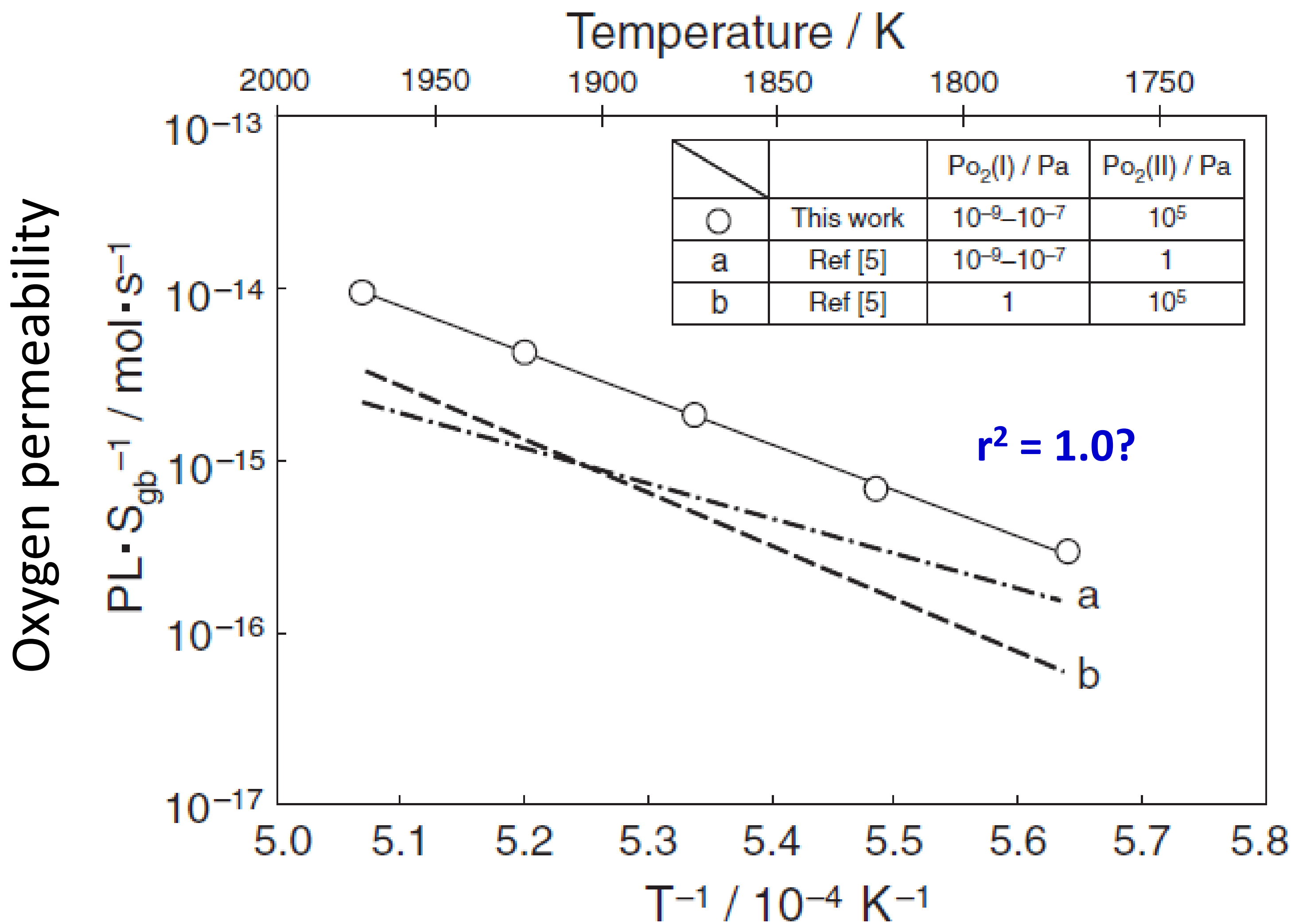
1-10^{-9} Pa
(Ar-H_2)



Vary I or II
Measure $P(H_2O)$
Measure $P(O_2)$
Calculate P, J, μ_O, δD_{gb}
(vs depth!)

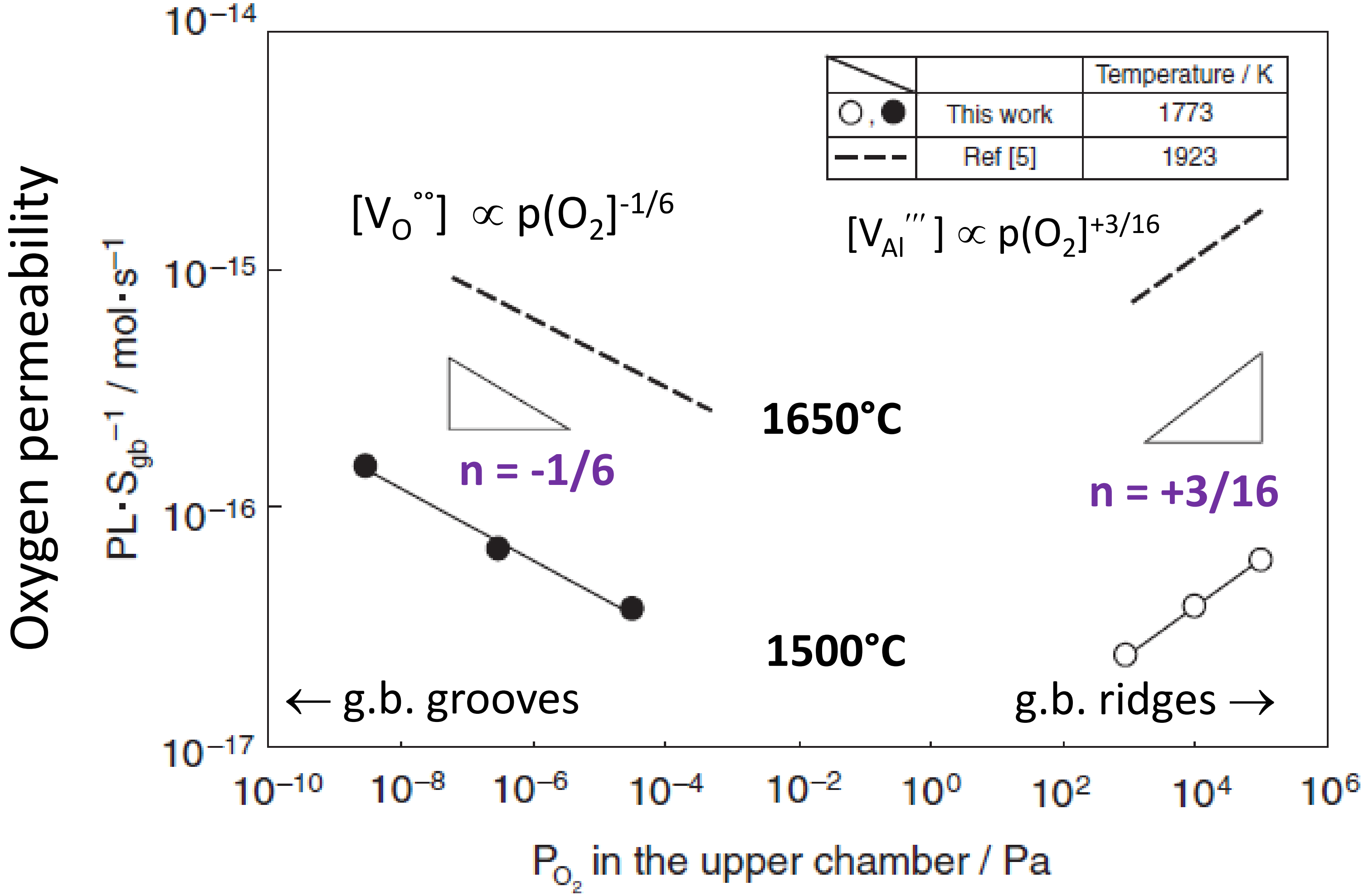
Alumina Permeability Studies: Temperature Effects

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839



Alumina Permeability Studies: $P(O_2)$ Effects

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839



δD_{gb} Measured from Alumina Permeability Studies

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839:

$$\delta D_{gb,O} = 2.207\times 10^{-9} \exp\left(\frac{-467\ kJ}{RT}\right)\left(P_{O_2,low}\right)^{-1/6} \quad m^3/s$$

$$\delta D_{gb,Al} = 2.475\times 10^{-5} \exp\left(\frac{-604\ kJ}{RT}\right)\left(P_{O_2,high}\right)^{3/16} \quad m^3/s$$

Wagner – Permeability Model (Oxygen)

$$k_{p,\mathrm{instant}} = \int_{P_{O_2},\mathrm{interface}}^{P_{O_2},gas} \frac{2A\exp(-Q/RT)}{G_i} P_{O_2}^{-1/6} d\ln P_{O_2}$$

Obtain $k_{p,i}$, δD_{gb} from eachother:

Oxygen (Primary) Contribution ($P_{O2,\ interface}$)

$$k_{p,i,O} = \frac{12\,\delta D^{W-W}_{gb,O,\,\mathrm{interface}}}{G_i}$$

$$or \quad k^{\times}_{p,i,O} = \frac{2\delta D^{\times}_{gb,O}\,\Delta \ln P_{O_2}}{G_i}$$

Aluminum Contribution ($P_{O2,\ gas}$)

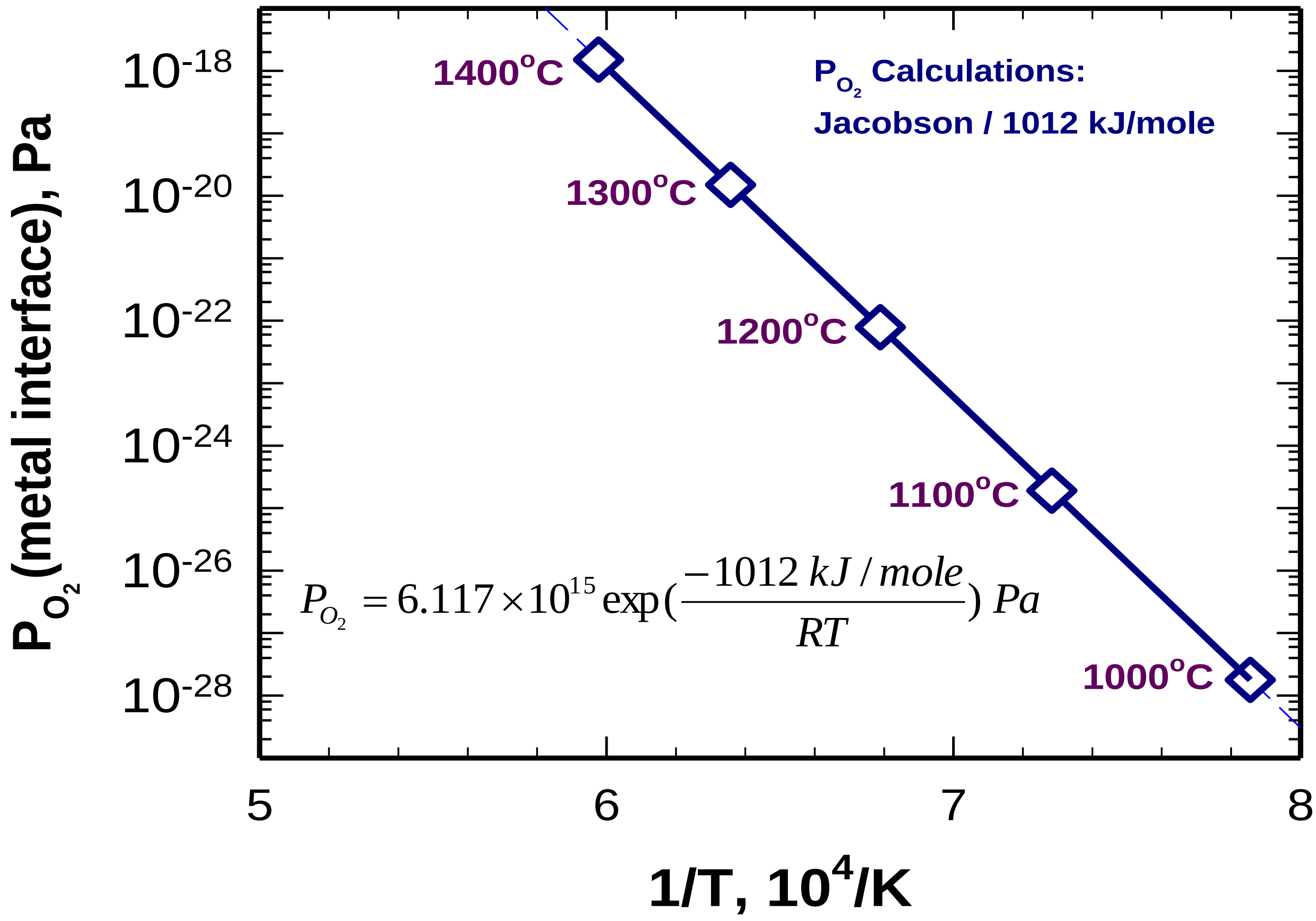
$$k_{p,i,Al} = \frac{16\,\delta D_{gb,Al,gas}^{W-W}}{G_i}$$

$$or \quad k_{p,i,Al}^{\times} = \frac{3\,\delta D_{gb,Al}^{\times}\,\Delta \ln P_{O_2}}{G_i}$$

Equilibrium $P(O_2)$ for FeCrAl(Zr) Oxidation Predictions

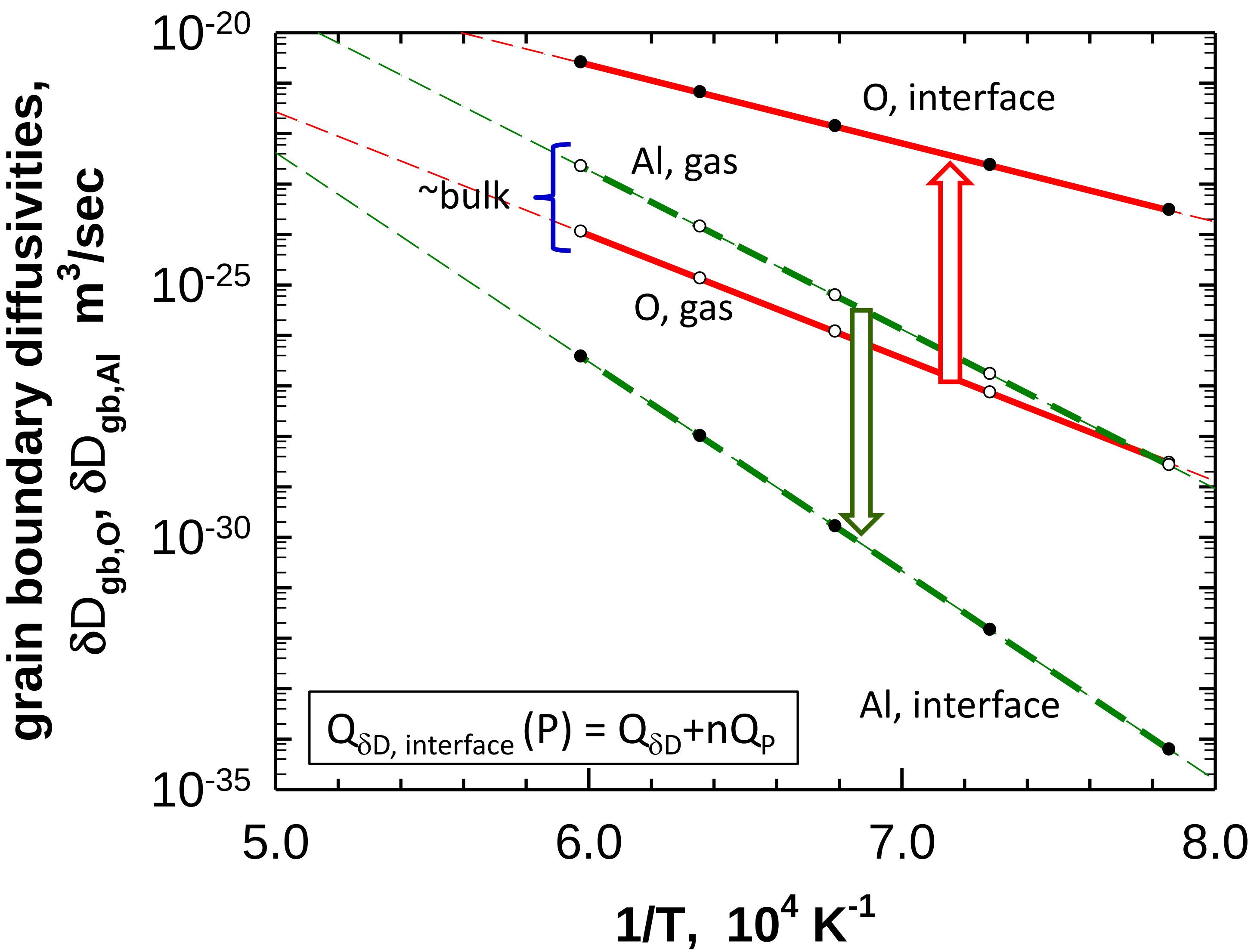
$$2Al + \tfrac{3}{2}O_2 = Al_2O_3$$

$$K_{eq} = 1/(a_{Al})^2(P_{O_2,equil})^{3/2}$$



Grain Boundary Diffusivity Product

Predictions for FeCrAl Scales vs Bulk Alumina



$$Q_{\delta D\ \mathrm{interface}} = Q_{\delta D,\ \mathrm{gas}} + nQ_{P,eq}$$

$Q_{P,eq}$ = 1012 kJ/mole

position	A_i (m^3/s)	Q_i (kJ/mole)	n_i
O, gas	4.23E-10	467	-1/6
O, interface	5.16E-12	**298**	-1/6
Al, gas	1.59E-04	604	+3/16
Al, interface	2.26E-02	**794**	+3/16

Measured k_p vs Predicted

(Permeability $\delta D_{gb,O}$)

$$\Pi_i = k_{p,i} \cdot G_i = 12\delta D_{gb,O,interface}$$

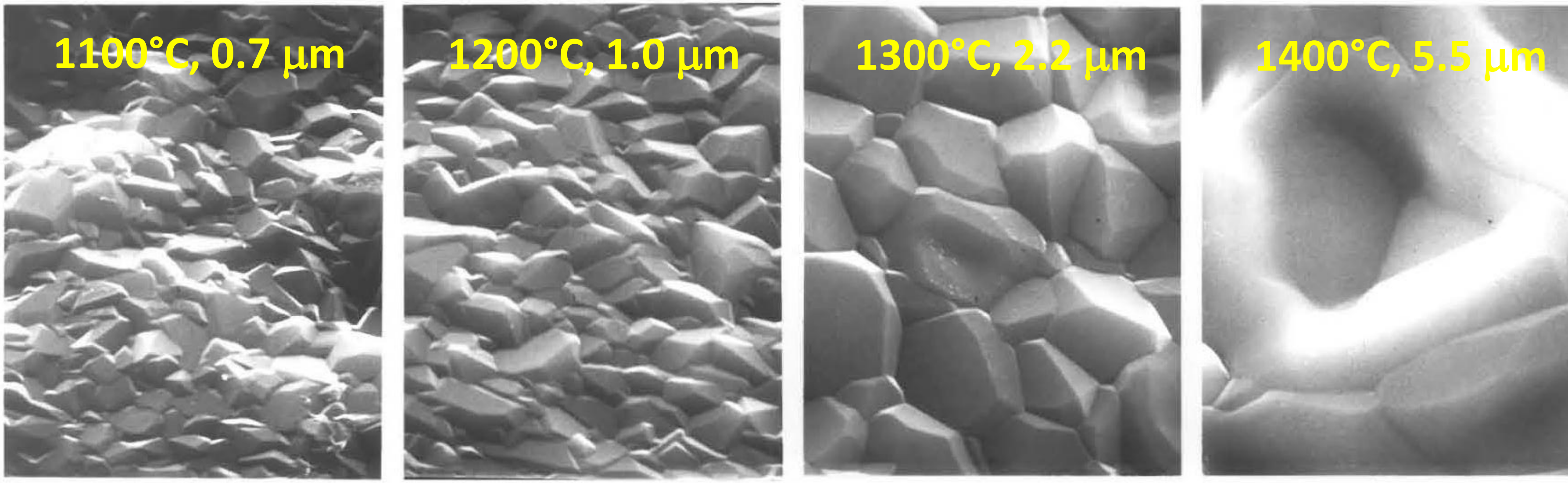
vs FeCrAl (Zr) Isothermal Oxidation

x_i (mg/cm^2), dx/dt, G_i for 25 samples

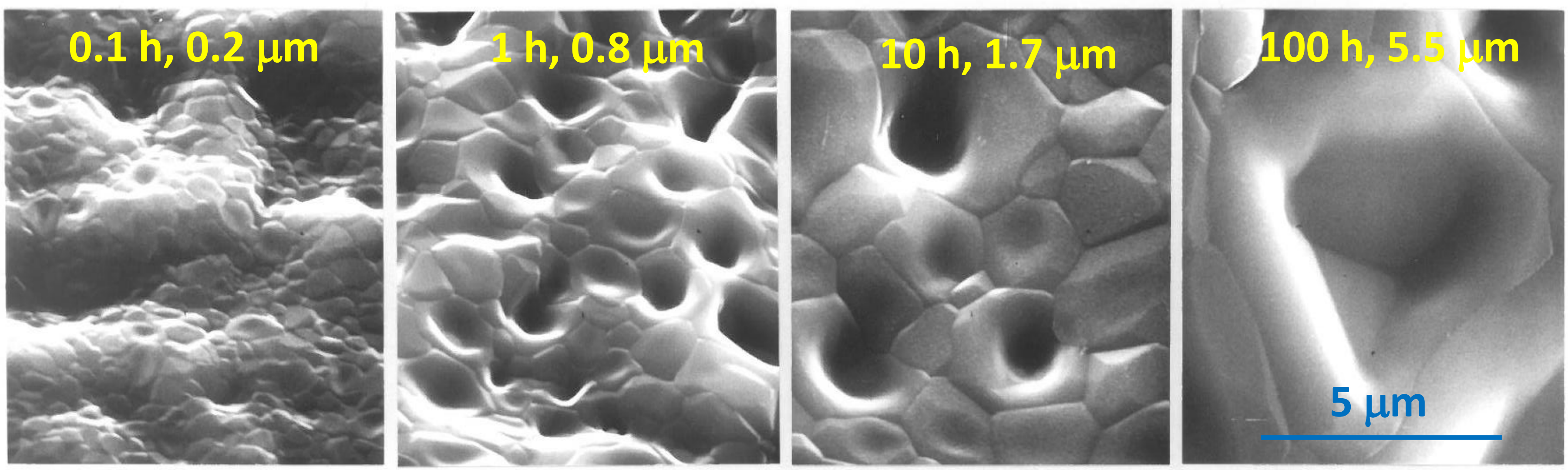
hours	1100°C	1200°C	1300°C	1400°C
0.1				
1				
10				
50				
100				
200				failed
500				
1000			failed	

Al_2O_3 Scale Underside Stripped from FeCrAl(Zr)

(A) 100 h

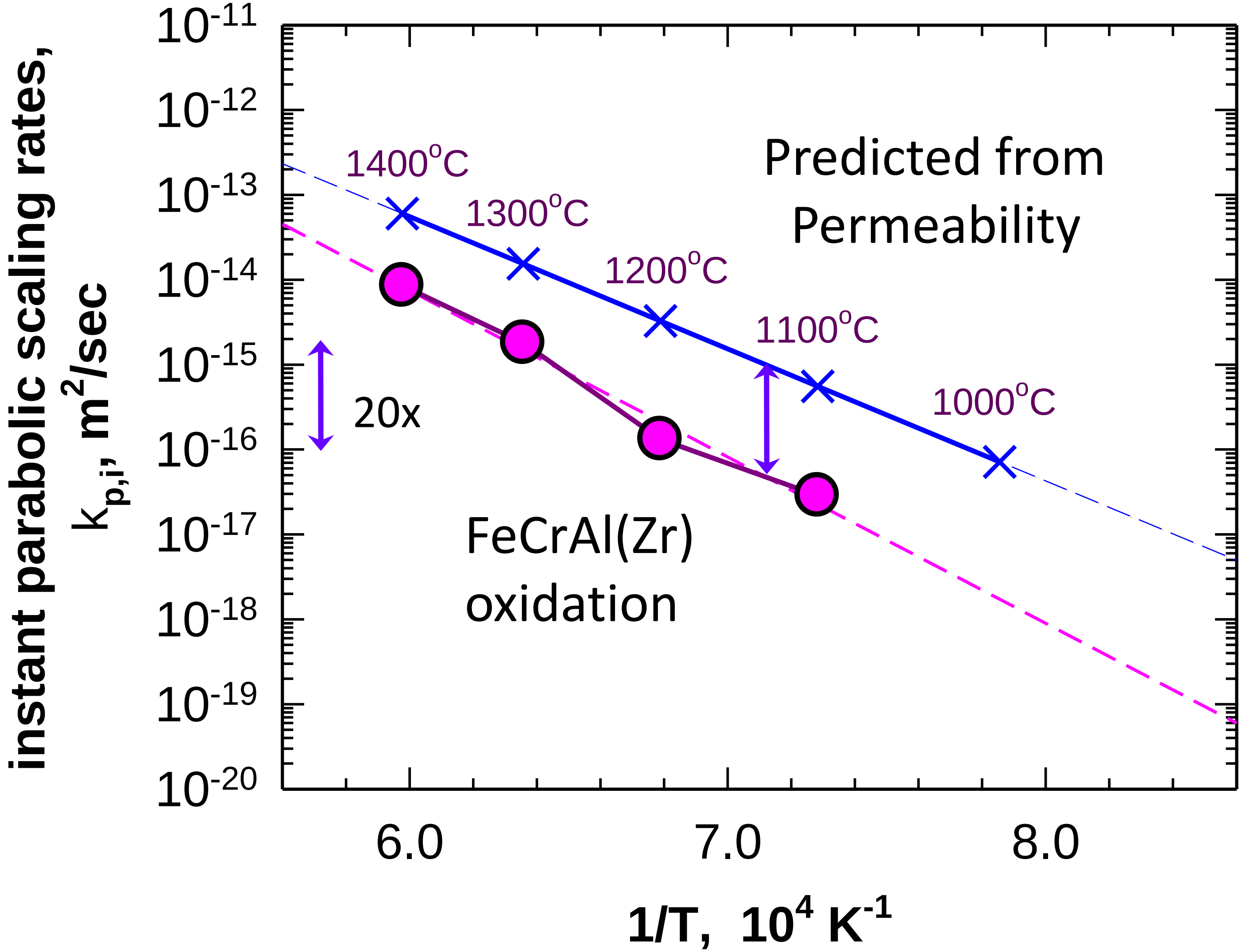


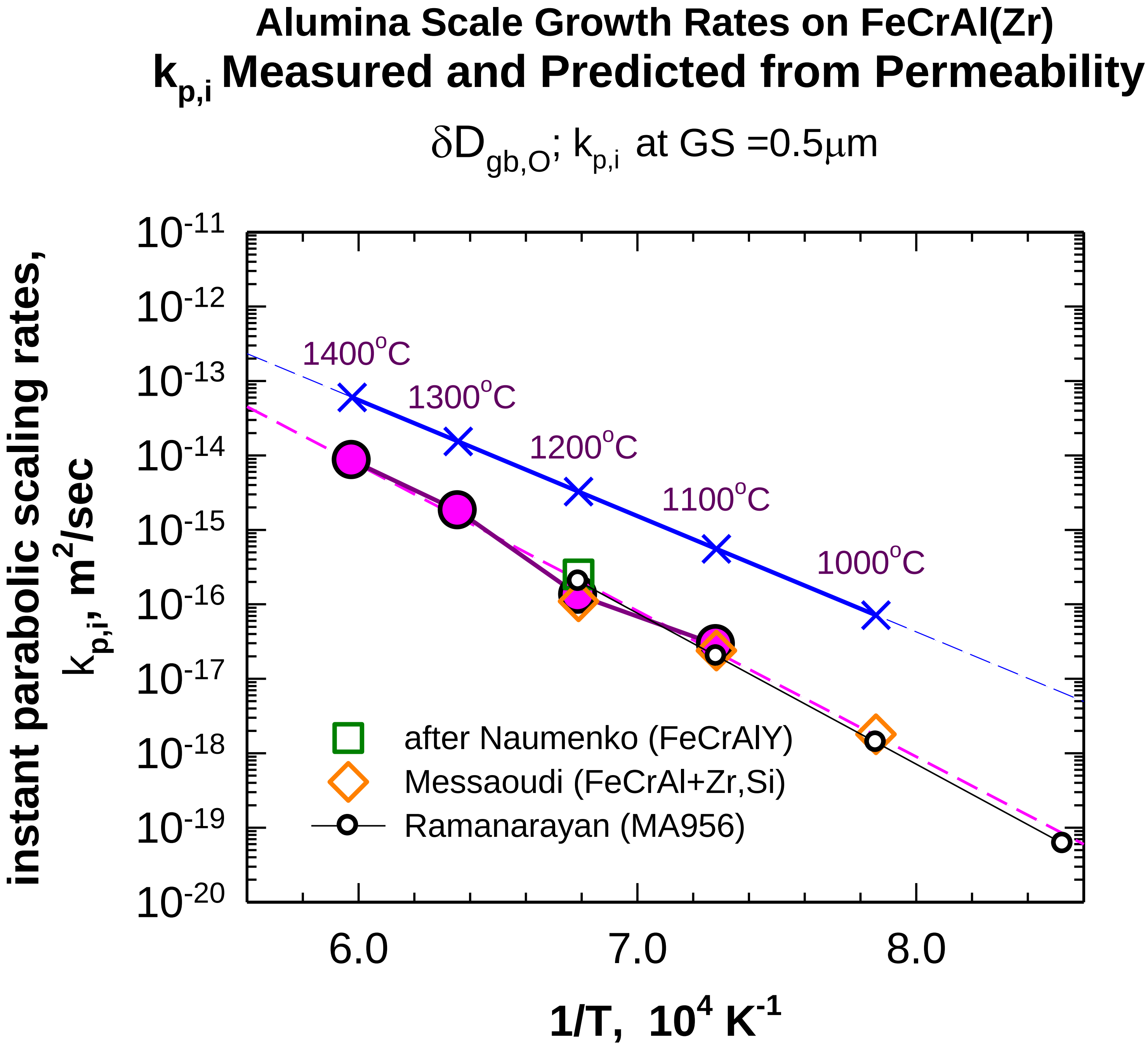
(B) 1400°C,



Alumina Scale Growth Rates on FeCrAl(Zr)
$k_{p,i}$ Measured and Predicted from Permeability

$\delta D_{gb,O}$; $k_{p,i}$ at GS =0.5μm

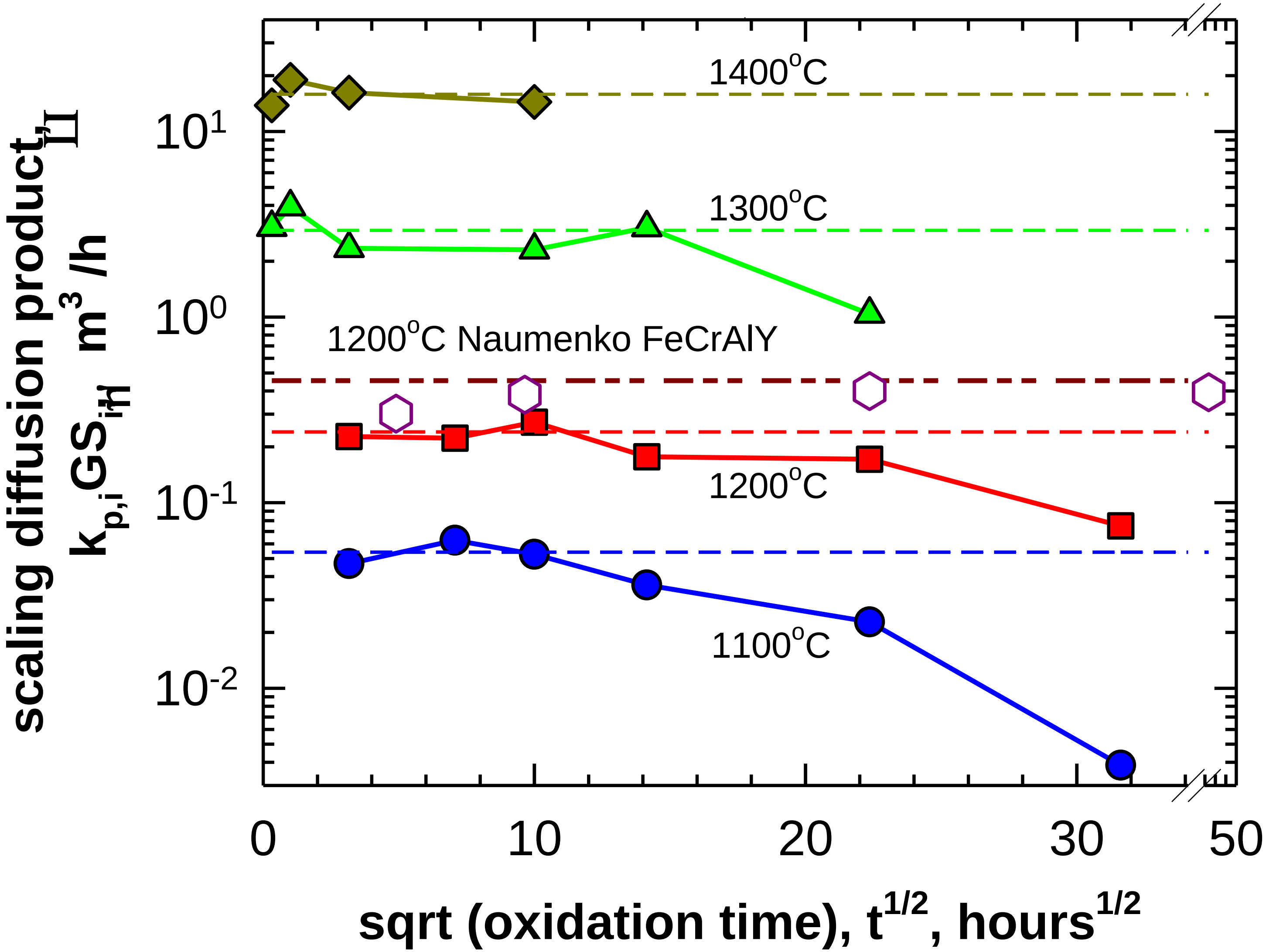



Alumina Scale Growth Rates on FeCrAl(Zr)
$k_{p,i}$ Measured and Predicted from Permeability
$\delta D_{gb,O}$; $k_{p,i}$ at GS =0.5μm
instant parabolic scaling rates,
$k_{p,i}$, m^2/sec
1/T, 10^4 K^{-1}
1400°C
1300°C
1200°C
1100°C
1000°C
after Naumenko (FeCrAlY)
Messaoudi (FeCrAl+Zr,Si)
Ramanarayan (MA956)
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
6.0
7.0
8.0

Predict $\delta D_{gb,O}$ from k_p

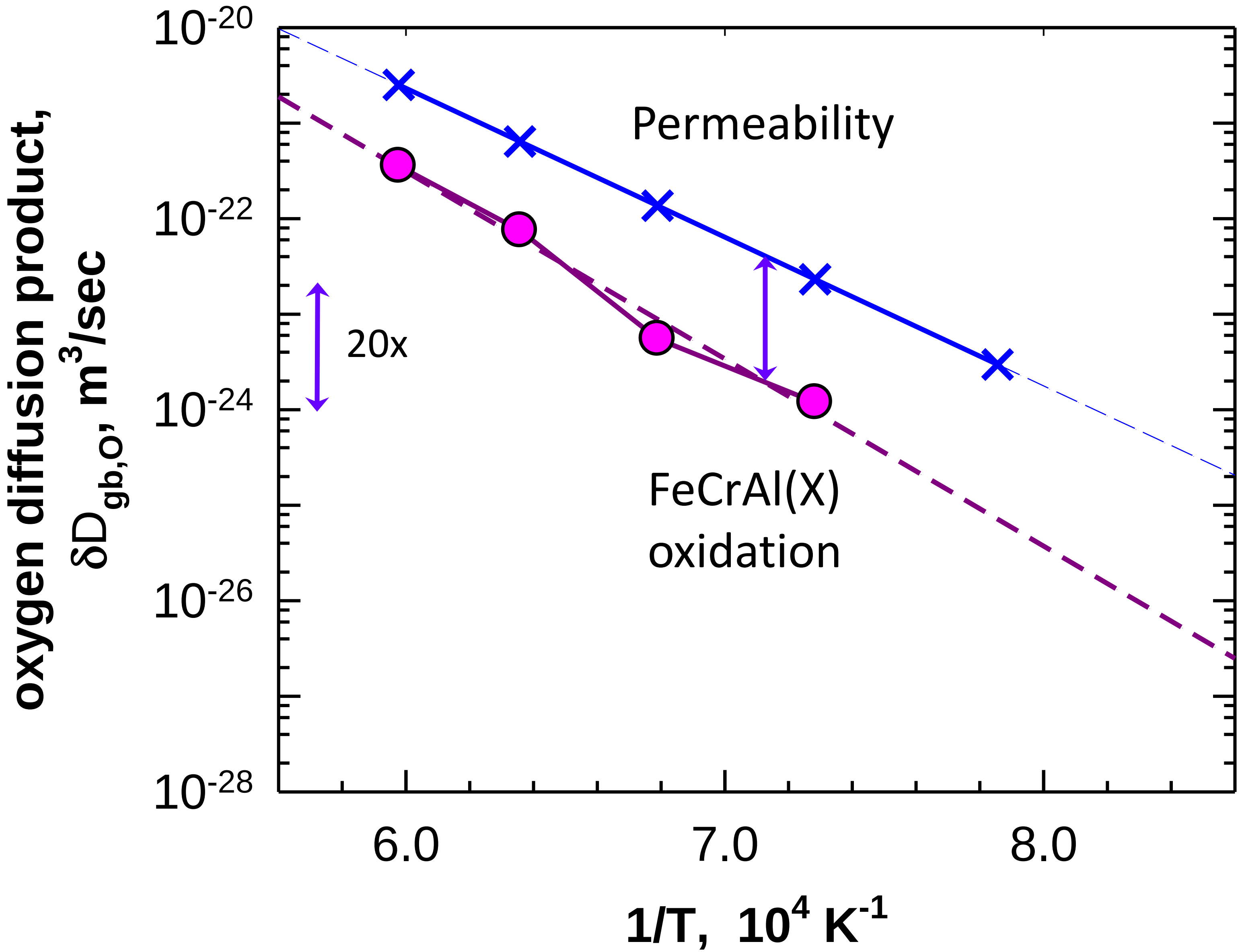
$$\Pi_i = k_{p,i} \cdot G_i = 12\delta D_{gb,O,interface}$$

"Invariant" Scaling Product, Π, from FeCrAlZr Oxidation Rates

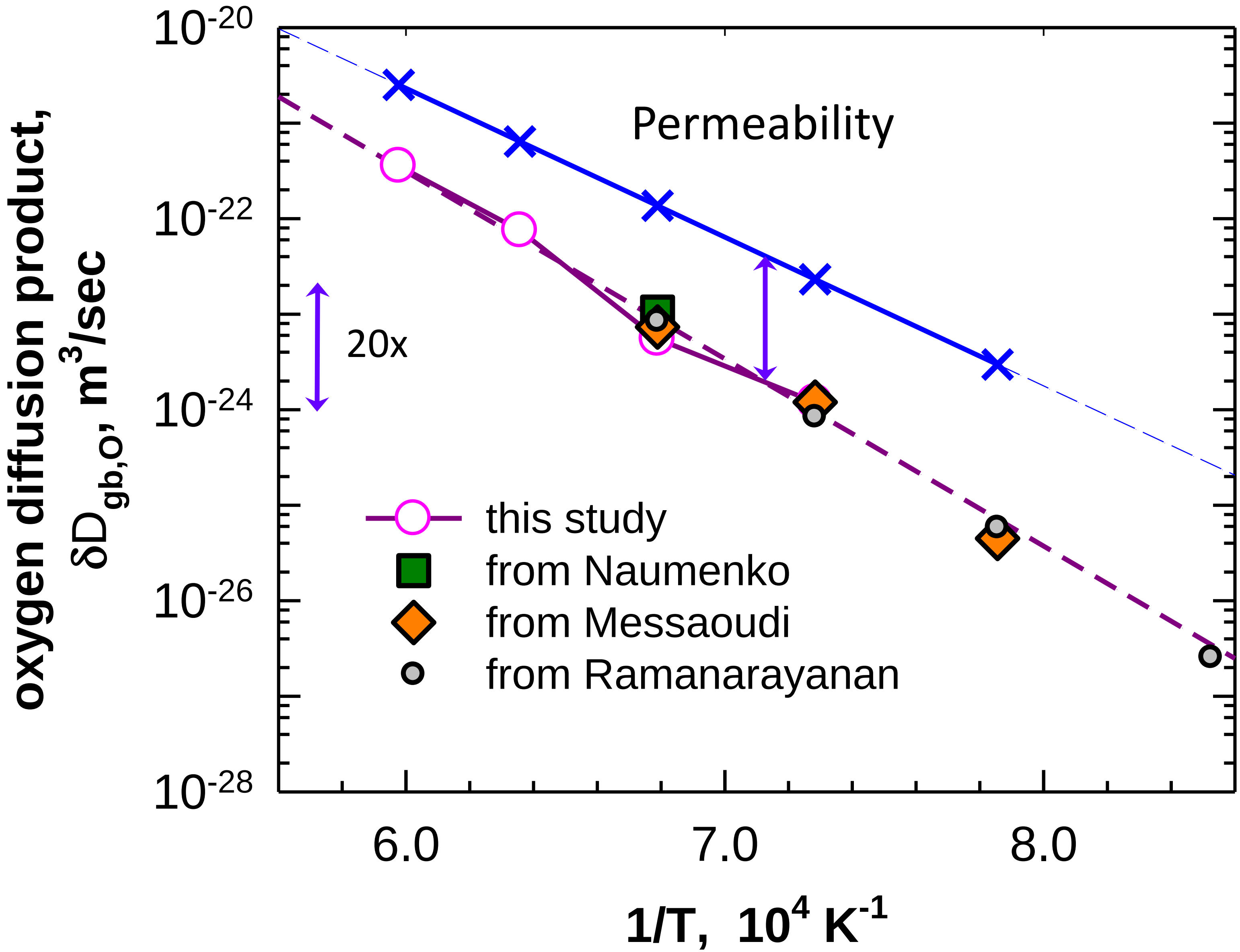


Scale Grain Boundary Diffusivity Product

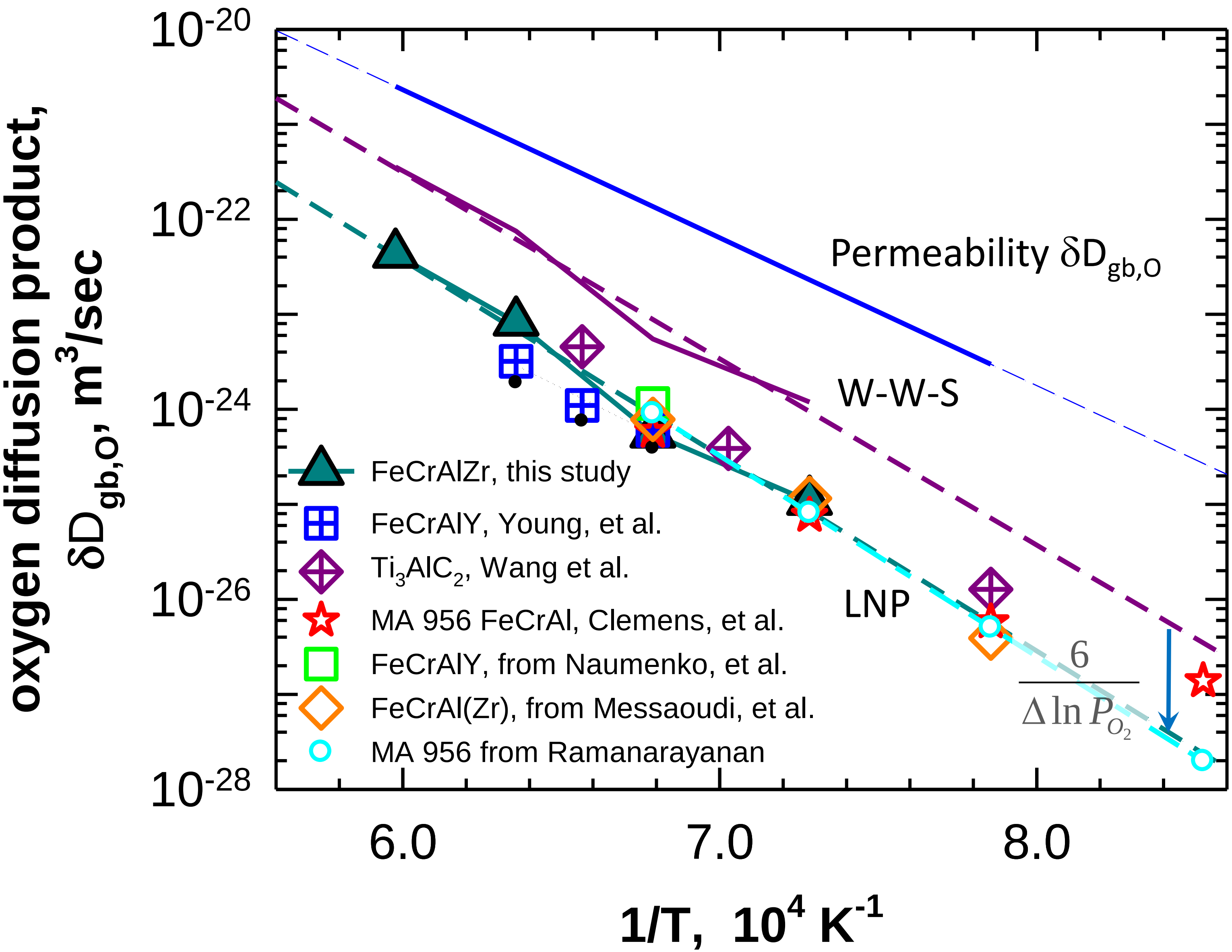
Oxidation Compared to Permeability Predictions



Scale Grain Boundary Diffusivity Product
Oxidation Compared to Permeability Predictions

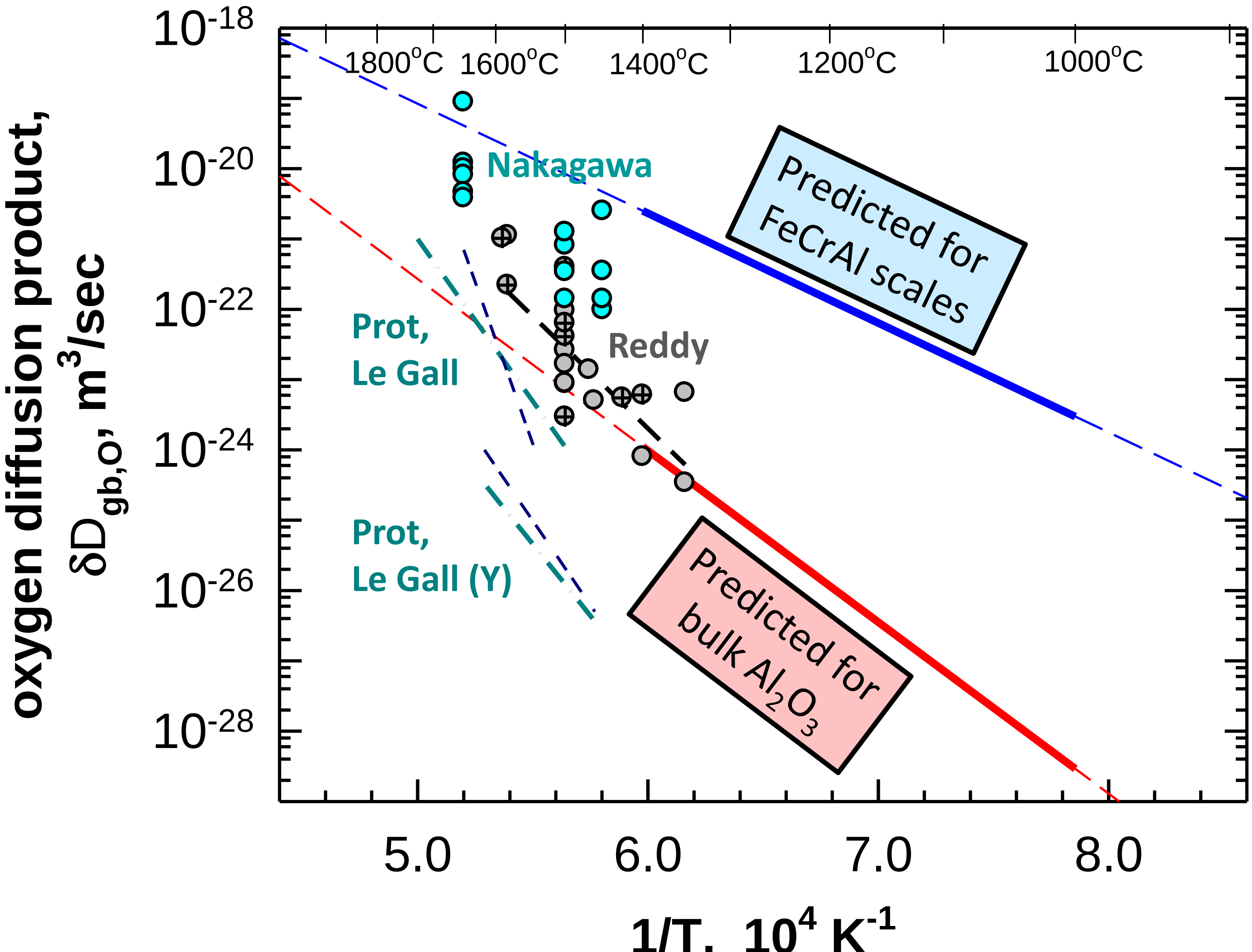


Scale Grain Boundary Diffusivity Product, $\Delta \ln P_{O2}$ solution
$\delta D_{gb,O}$ from Oxidation (FeCrAl(X), Ti_3AlC_2)

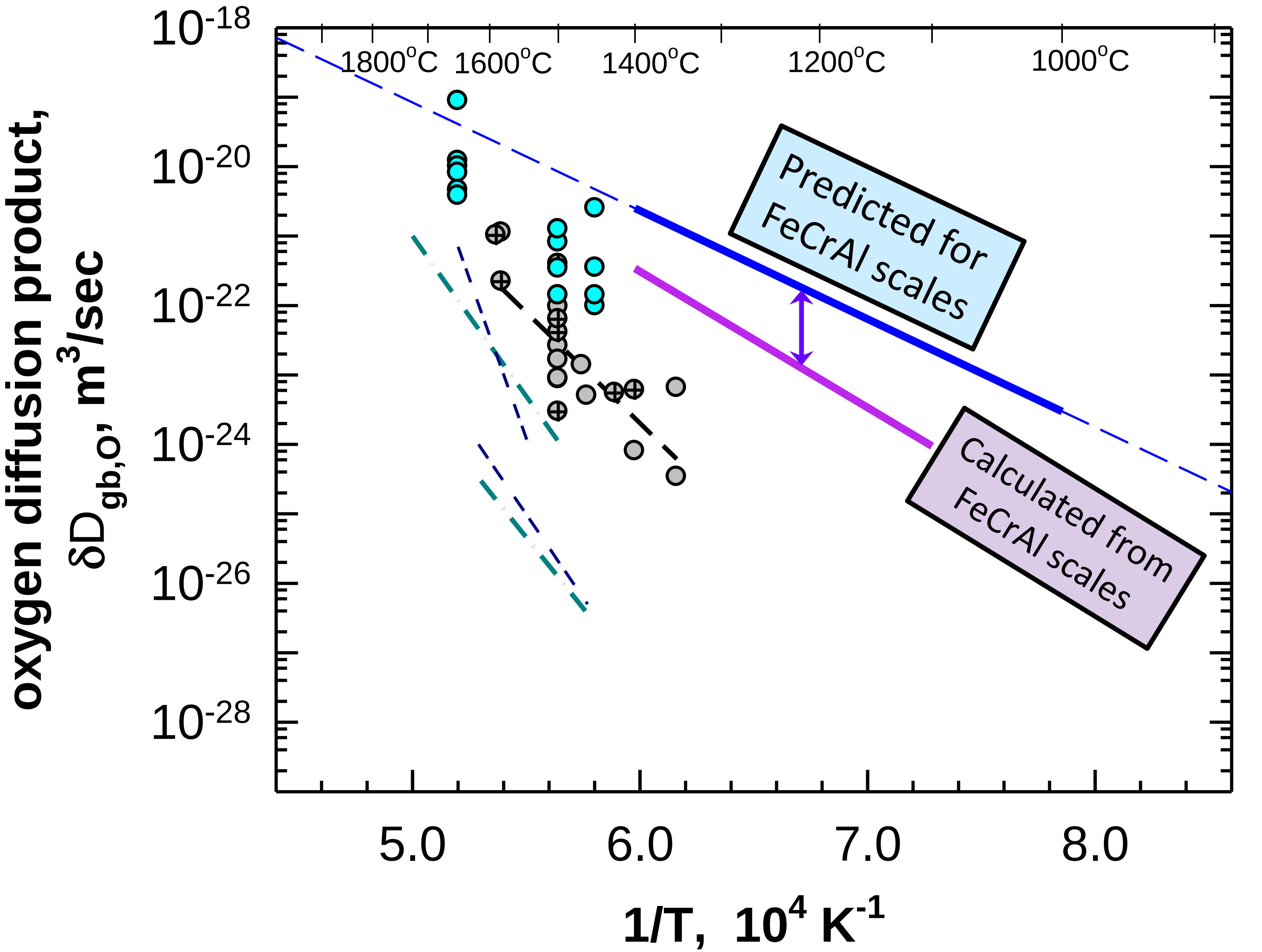


Alumina Grain Boundary Diffusivity Product

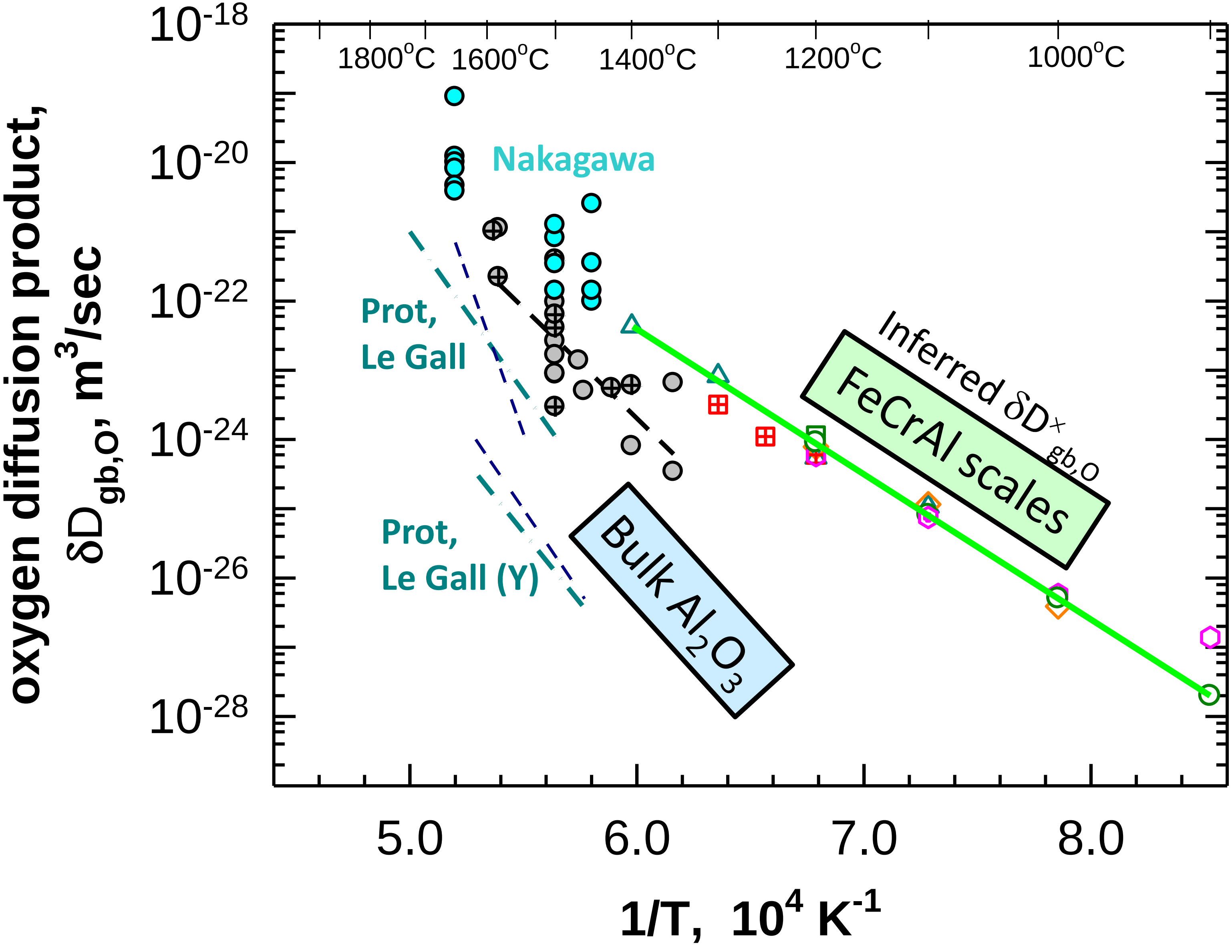
Bulk ^{18}O Tracer vs Permeability



Alumina Grain Boundary Diffusivity Product
Bulk ^{18}O Tracer vs Permeability - Oxidation

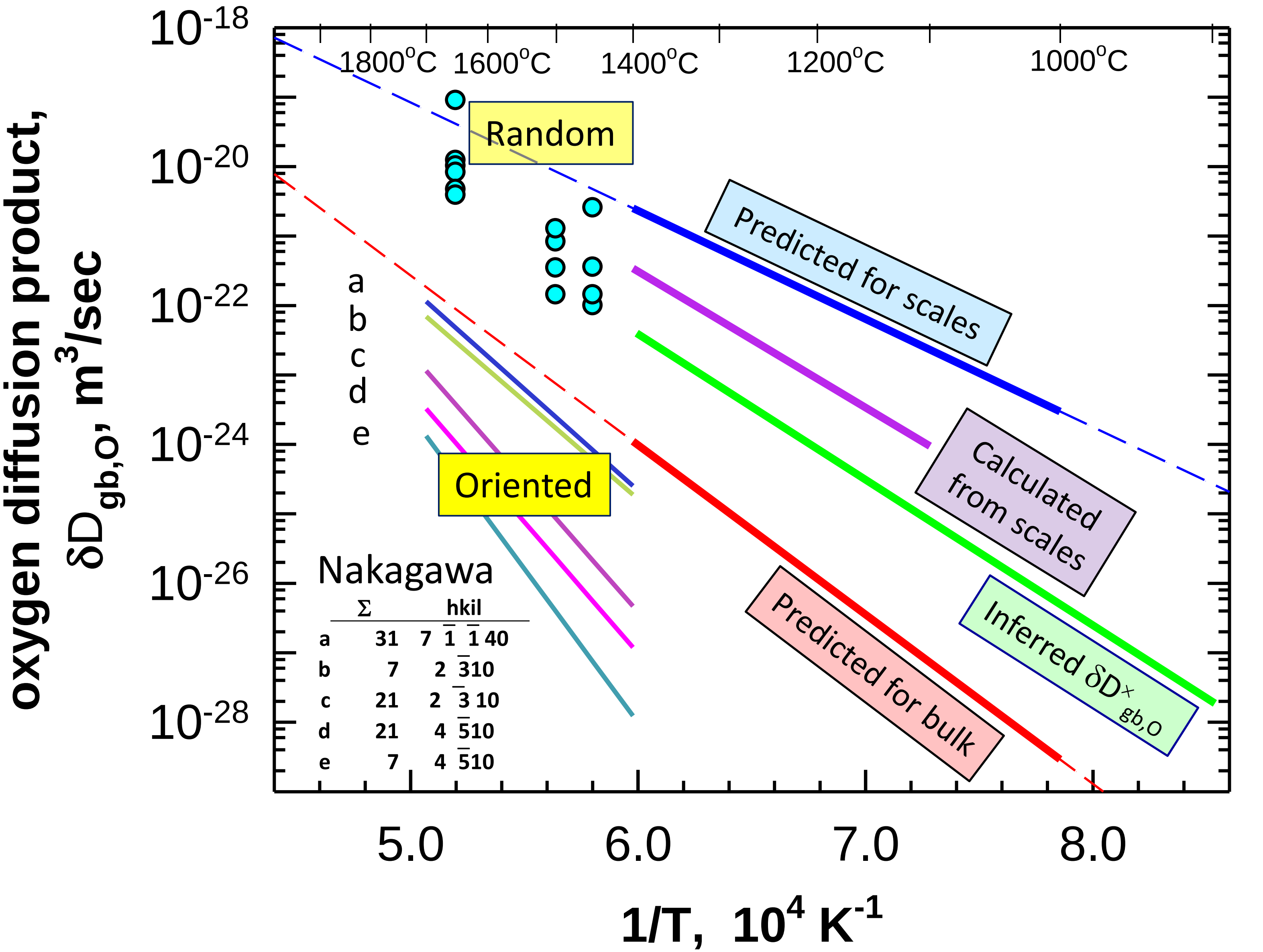


Alumina Grain Boundary Diffusivity Product
Wagner Oxidation Compared to Bulk ^{18}O Tracer



Alumina Grain Boundary Diffusivity Product

Bicrystal ^{18}O Tracer vs Permeability/Oxidation



Dopant Effects from Permeability Analyses

Matsudaira, Wada, Saitoh, Kitaoka

- Lu reduces δD_{gb} (oxygen) by 5x
- Hf reduces δD_{gb} (aluminum) by 3x
- Lu + Hf increase δD_{gb} (Al and oxygen) by 2x

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

Bulk values (1 atm) should not agree

with scale values (10^{-33}-10^{-23} atm):

Predicts $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$

- **Interface (Oxygen): $\delta D_{gb,O}$ and $[V_O^{\circ\circ}] \propto (p_{O2})^{-1/6}$**
- **Gas surface (Aluminum): $\delta D_{gb,Al,}$ and $[V_{Al}^{'''}] \propto (p_{O2})^{+3/16}$**
- **$\delta D_{gb,O} >> \delta D_{gb,Al}$**

Alumina Scale Growth Mechanisms: **Some New Attractions from Permeability Analyses**

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}$ $[V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}$ $[V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$

Oxidation Constant, Π, Gives Oxygen Diffusivity:

$$\Pi_i = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$$

(and vice versa)

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}$ $[V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}$ $[V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$
- $\Pi_I = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$

$$\mathbf{Q_{interface} = Q_{1\ atm} + 1/n\ Q_{P(equilibrium)}}$$

298 = 467 - 1/6 (1012) kJ/mole

375 = measured from scales

Alumina Scale Growth Mechanisms: **Some New Attractions from Permeability Analyses**

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}$ $[V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}$ $[V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$
- $\Pi_l = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$
- 298 kJ/mole predicted for scales; 375 kJ/mole measured for scales

Highly Variable $\delta D_{gb,O}$ Bulk ^{18}O Measurements

(Tsubasa Nakagawa, et al., U. Tokyo; CWRU)

$\delta D_{gb,O}$ (random) up to 10^8 $\delta D_{gb,O}$ (bicrystal)

$\Sigma 7$, $(45\bar{1}0)$ hkil

Alumina Scale Growth Mechanisms: **Some New Attractions from Permeability Analyses**

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}$ $[V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}$ $[V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$
- $\Pi_I = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$
- 298 kJ/mole predicted for scales; 375 kJ/mole measured for scales
- $\delta D_{gb,O}$ (random) = $10^8\ \delta D_{gb,O}$, $\Sigma 7$, $(4\bar{5}10)$ hkil bicrystal